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Novel High-Activity Organic Piezolectric Materials - From Single-Molecule Response to Energy Harvesting Films

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14. ABSTRACT
There is a critical need for efficient energy harvesting materials to use ubiquitous but wasted mechanical energy. There is also a simultaneous need for micro- and nano-electronic energy generation and conversion for self-powered sensors, haptic displays, and responsive shape-changing materials. With this project, we have established that dramatic improvements can be found in piezoelectric materials designed from the geometric conformational change in single molecules, driven by electric field gradients. This project designed accurate, efficient quantum chemical methods to efficiently predict the piezoresponse of conventional hydrogen-bonded organic crystals and polymers. Using these methods, we determined a theoretical maximum for conventional organic piezoelectrics and devised molecular springs with predicted response far exceeding ZnO or PVDF. Investigating different molecular scaffolds, we designed single-molecule ferroelectrics with stable hysteresis and piezoelectric response predicted on par with champion perovskites. We demonstrated this potential with the first measurements of the piezoelectric response of single molecular monolayers. Moreover, using a polyurethane foam matrix and a polar dopant, we made flexible piezoelectric films over ten times greater than ZnO.

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AFSOR Final Performance Report

Project Title:	**Novel High-Activity Organic Piezolectric Materials - From Single-Molecule Response to Energy Harvesting Films**
Award Number:	**AFOSR grant FA9550-12-1-0228**
Start Date:	May 15, 2012
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Accomplishments/New Findings:

- Efficient quantum chemical methods were developed to accurately predict the piezoelectric response of organic hydrogen-bonded crystals and single-molecule electromechanical response. Using the known piezoelectric response of crystalline 2-methyl-4-nitroaniline, computational predictions were within 10% of experiment. Moreover, predictions suggested that in multi-layer films, the parallel alignment of molecular dipole moments strongly increases the piezo-response.

- We determined that ubiquitous polar hydrogen bonds are piezoelectric. Studying conventional organic piezoelectric crystals and polymers (e.g., polyvinylidene difluoride, PVDF) revealed a theoretical maximum for the piezoelectric response in such materials (d_{33} ~45 pC/N).

- Large piezoelectric response were computed for conjugated “molecular spring” compounds, including substituted [6]helicenes, with predicted charge and current ~2-3x greater than conventional ZnO or PVDF materials (i.e., d33 50-60 pC/N) and exceeding the theoretical maximum in hydrogen-bonded crystals.

- Computational studies of related molecular springs predict charge and current ~4-5x greater than ZnO or PVDF materials (i.e., ~100 pC/N) by nitrogen substitution and increased dipole moments. The fundamental properties required for immense molecular piezoelectric response include large dipole moment, large polarizability, and low force constant vibrational breathing modes.

- Using computational exploration of the electromechanical response other molecular scaffolds, we explored single-molecule ferroelectrics based on bowl-shaped aromatic hydrocarbons with stable hysteresis effects, controllable barriers to interconversion, and extremely high piezoelectric response (>400 pC/N) on par with champion perovskite ceramics such as lead zirconium titanate (PZT). By modulating the functionalization and the bowl curvature/depth, both the ferroelectric interconversion barrier and piezoelectric response can be modulated.

- The piezoelectric response of single molecular monolayers was measured using piezo-force atomic force microscopy (PFM). Using patterning and statistical techniques, we determined that helical oligoalanine peptides showed conformational changes in response to an applied electric field, far greater than control molecules. This technique is now a reliable screening method for new molecular piezoelectric materials.

- Inherently flexible organic piezoelectric films were fabricated using polyurethane foams doped with varying concentrations of 2-chloro-4-nitroaniline. After poling with an applied electric field, the polymer foams yielded immense d_{33} response exceeding 250 pC/N, ***over ten times the generated charge*** of comparable ZnO and PVDF materials. Increasing the dipole moment of the dopant, the concentration of dopant, poling field, and decreasing the elastic modulus of the polymer all increase the piezoelectric response.

Summary:

We have designed organic molecular piezoelectric materials with dramatically increased response and energy generation properties compared to conventional ZnO and polyvinylidene difluoride (PVDF). Dramatic advances in organic electronic materials with promise for lightweight, flexible devices and applications from touch sensors to medical implants have not been matched with solutions for energy storage, conversion and generation. The promise of organic *piezoelectric* materials is the ability to design and optimize properties including piezoresponse, elastic modulus, electrical properties, and processability.

We established that this new category of molecular organic piezoelectrics yields tremendous breakthroughs in response, ***with over ten times the charge generation of ZnO and PVDF*** using both experiments on single-molecule monolayers and thin-film materials and computational exploration. The combined research found targets for future synthesis and developed accurate nanoscale characterization techniques.

In collaboration with Prof. Daniel Lambrecht at the University of Pittsburgh, we designed highly accurate computational methods to predict the piezoelectric response of organic crystals and "molecular springs." Importantly, we find that ubiquitous hydrogen bonds can be significantly piezoelectric.

Moreover, we uncovered a theoretical maximum to the piezo-response in PVDF and similar crystals that limited previous efforts to match the properties of inorganic materials. Instead, we designed molecular springs based on helical conjugated molecules with predicted piezo-response and generated charge ~2-3 times greater than ZnO and PVDF. Further computational exploration has led to understanding the fundamental properties required to exceed even champion perovskite ceramics. We found conformational distortions that lead to single-molecule ferroelectrics with controllable interconversion barriers and immense piezoelectric response.

Building on these computational efforts, we experimentally determined the piezoelectric response of single molecular monolayers of short oligopeptides. Our method uses piezo-force microscopy (PFM) to characterize patterned monolayers, and establishes the response derives from the conformational change of the peptide helix. The results suggest that many proteins are piezoelectric, with continuous linear distortion in response to an electric field, strikingly different from conventional "switches" in light- or redox-driven molecular motors.

Highlighting the inherent flexibility of organic materials, we used a commercial polyurethane foam matrix and doped with the polar 2-chloro-4-nitroanline molecule. Using a low elastic modulus open-cell foam and a high concentration of dopants, we poled the films to produce force sensors exceeding 250 pC/N, ***over ten times the generated charge of ZnO and PVDF.*** Measured electrical current density *exceeds 0.4 mA/m^2 in a 1.0 cm^2 device*.

Based on the nearly infinite variety of organic molecules, materials based on these molecular design strategies have already exceeded conventional energy harvesting piezoelectrics. The fundamental theoretical limit for piezoelectric response in organic molecular materials far exceeds champion ceramics due to the lower dielectric constant and elastic modulus. Moreover, the use of inherently polar self-assembled multi-layers allows facile patterning and increased stability compared to ceramics. To further improve on these groundbreaking efforts, synthetic targets will need to possess large molecular dipole moments, large polarizability, low elastic modulus, and small vibrational force constants. Several such targets have been identified for future research.

Efficient, Accurate Quantum Chemical Prediction of Organic Piezoelectric Response

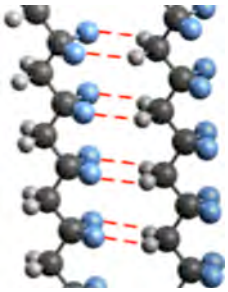

Fig 1. PVDF

We speculated that the piezoelectric response in PVDF polymers and other organic solids with polar order derives from deformations among intermolecular hydrogen bonds (**Fig. 1**). H-bonds are weak polarizable electrostatic interactions and consequently should deform easily in an applied field. We tested this hypothesis with a collaborator, Daniel Lambrecht (Pitt), using computational predictions of the geometric distortion under an applied electric field. Using approximate MP2 quantum chemical methods on molecular clusters of 2-methyl-nitroaniline (MNA) (**Fig. 2**) we found outstanding agreement between computed piezoresponse and experiment[1] (determined by x-ray analysis).[2] ***Our results indicate that polar hydrogen bonds, ubiquitous across chemistry and biology, are often piezoelectric and can deform significantly in the presence of nanoscale electric fields.***

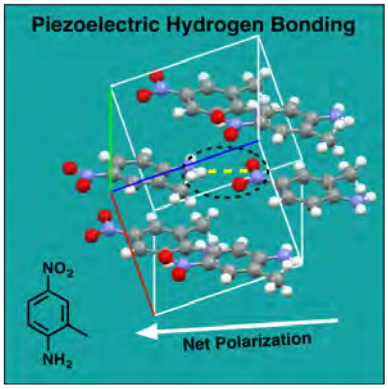

Fig. 2. Molecular structure of 2-methyl-4-nitroaniline, a known organic crystalline piezoelectric, illustrating the hydrogen-bond interaction in the solid.

A further collaborative effort led to a signficant speed increase in calculating piezoelectric response. Investigating a set of hydrogen-bonding molecules suggests a fundamental limit to the piezoelectric response of H-bonds[3] that arises from a tradeoff between the electrostatic polarizability and the strength of the interaction. Weak H-bonds are easy to deform, but tend to have small partial charges and polarize little in response to an electric field. Strong H-bonds tend to have large partial charges and polarize significantly in response to an electric field, but in turn have high force constants and are difficult to distort. Our results suggest that while some hydrogen-bonding solids (including MNA and PVDF) are known to be piezoelectric, a theoretical maximum of ~50 pm/V exists. This previously-unknown limit has clearly prevented previous efforts to create piezoelectric organic solids and polymers.

Computational Exploration of Conjugated Molecular Springs

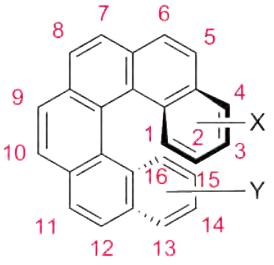

Fig. 3 [6]Helicene piezoelectric molecular spring

While hydrogen-bonded solids are limited in their piezoelectric response, we can design molecular springs with low force constant vibrational breathing modes. We explored the computed piezoelectric response of π-conjugated helical molecules using density functional theory (DFT) calculations. Notably the [6]helicenes seen in **Fig. 3**, undergo remarkable deformation under an applied electric field. The deformation is driven by conformational changes, rather than direct stretching of the covalent bond framework.[4] At fields of 1 V/nm, covalent carbon single bonds are predicted to distort less than 0.05 Å, or ~0.4% of the bond length. In contrast, these molecules exhibit a ~10-12% change in distance along the deformation direction. Importantly, while such fields are large in macroscopic terms, they are still small on an atomistic scale, corresponding to +/- 0.002 atomic units, or the field due to only a single positive or negative charge, ~1 nm from the molecule.

Predicted piezoelectric coefficients (d_{33}) from our initial study range as high as 46-60 pC/N (= pm/V), far beyond ZnO, PVDF and other existing organic materials (10-30 pC/N), as indicated in ***Table 1***.[27,62,63] We have already computed the piezoresponse with a variety of possible synthetic modifications, such as functional groups, helical scaffold, and regiochemical substitution, to the basic helicene. Thus we can directly correlate changes in molecular structure with improved piezoresponse. For example, steric repulsion of substituents in certain positions decreases the overall deformation. Also, one might naïvely expect that the molecular dipole moment would be the most important predictor of the piezoelectric coefficient, since it governs the interaction energy between the molecule and the applied electric field. Instead, we find the polarizability (and thus the induced dipole moment) correlates better.[4]

Table 1. Approximate figures of merit for select piezo materials.

Material	Piezo Coefficient (d_{33} in pC/N)
$Pb(Zr,Ti)O_3$ - PZT	~250-500
ZnO	~20-30
Poly(CH_2CF_2) - PVDF	~10-20
Helicenes	~40-60 (predict)

Beyond these first-generation molecular springs, we explored the systematic substitution of nitrogen, oxygen, and sulfur heteroatoms in the helicene backbone. In particular, the use of nitrogen susbtitution in key positions dramatically increases the predicted piezorespone from 48 pC/N to 105 pC/N (**Fig. 4**). Use of 5-membered thiophene, pyrrole, or furan rings along the backbone significantly distort the helical shape and do not allow favorable alignment of the donor (amine) and acceptor (nitro) groups. Adding additional donor and acceptor groups also leads to increased computed piezoelectric coefficients, proportional to the increase in molecular dipole moment.

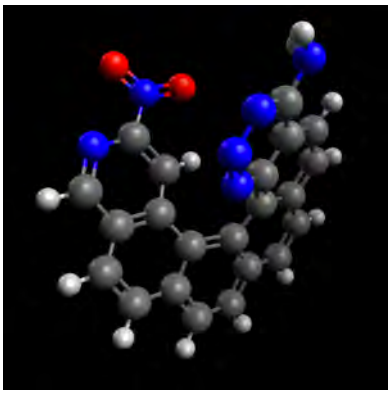

Fig. 4 Substituted azahelicene

In short, the computational exploration of molecular spring motifs incdicates clear structure/property correlations with the molecular dipole moment, polarizability, and vibrational force constants. The key figure of merit, the d_{33} piezoresponse can be understood by unit analysis:

$$d_{33}\ (\mathrm{pC/N}) \equiv (\mathrm{pm/V}) = \frac{(\%\ \mathrm{deformation})}{(\mathrm{applied\ field})} \qquad (1)$$

That is, 500 pC/N = 500 pm/V, or a 50% change in length at an applied field of 1.0 V/nm. For example, a molecule exhibiting a change in length from 4Å to 6Å under an applied field of 1.0 V/nm, or a smaller molecule lengthening from 2Å to 3Å would both yield d_{33} = 500 pC/N, far beyond ZnO or PVDF. ***Consequently, we believe the fundamental limit to molecular piezoelectric response to exceed 1000 pC/N, over 40x greater charge generation.***

Computational Discovery of Single-Molecule Ferroelectric Response

The key design principal in this project is that many polar molecules change geometric conformation in response to an applied electric field. Consequently, beyond helical molecules, we explored other molecular shapes, including π-conjugated "bowls." In such systems, not only is the molecule piezoelectric, but also ferroelectric. The polarization inversion relies on the conformational change, unlike traditional counterparts in which ferroelectricity originates from the switch of an asymmetrical polar unit cell in inorganic crystals, mobile hydrogens or ions in organic crystals, or from the polar polymer chain rotation of ferroelectric polymers.

As indicated in **Fig. 5**, an applied electric field couples to the molecular dipole moment and induced dipole, adding sufficient potential energy to the system to interconvert the buckybowl between "up" and "down" states. We find the inversion barrier, given by the completely planar aromatic system varies with the fourth power of the bowl depth, and between ~1-100 kJ/mol. Control over the curvature of the hydrocarbon and substitution of multiple polar substituents modulates the barrier. Moreover, since the bowl depths are ~1 Å, such an geometric inversion can lead to an incredibly large piezo-response given by Equation 1.

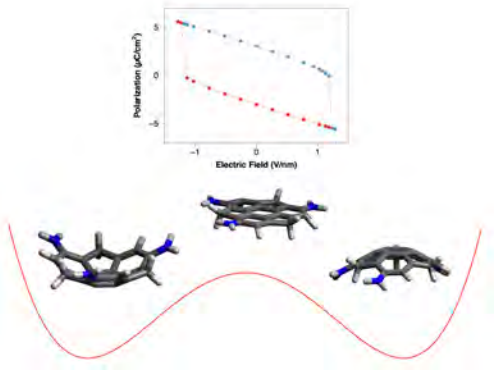

Fig 5. Computed response of single-molecule ferroelectric substituted sumanene.

For example, the compound with lowest inversion barrier (**Fig. 6**), a substituted perylene is also predicted to yield a piezoelectric response of 450 pC/N. While the tetra-nitro analogue is likely unstable, multiple analogues are computed to yield similarly large piezoelectric response. Since the quantum calculations are performed at zero temperature, thermal corrections and the zero-point vibrational energy decrease the inversion barrier significantly. Consequently several targets are attractive for future synthetic investigation. The study also demonstrates that beyond molecular springs and bowl shapes, new scaffolds for conformationally-driven piezoelectric response are likely, with unique properties.

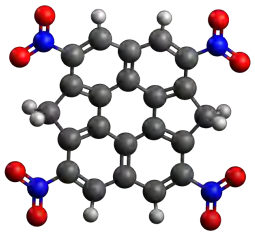

Fig 6. Substitued perylene with low bowl inversion barrier and large piezoresponse.

Experimental Characterization of Single Molecular Monolayer Piezoelectrics

Our molecular piezoelectrics operate on the concept that the geometry and conformation of polar molecules changes under an applied electric field. As a proof of principle of our molecular piezoelectrics, we recently measured the piezoelectric response of *single monolayers* (~1 nm) of oligopeptide films for the first time.[5] We used simple solution-based microcontact printing techniques to deposit and pattern intrinsically polar self-assembled monolayers (SAMs) on smooth template-stripped gold films through the cysteine thiol-gold interaction. Using established piezo-force AFM (PFM) techniques[6-9] to image both the topography (height) of our films, and the piezoresponse, we observed significantly greater piezo-response for the patterned peptide SAM (CA_6) compared to dodecanethiol (DT) using the bare gold regions as a built-in baseline (**Fig. 7**).

Since the measurements are performed in ambient conditions, some fraction of the carboxylate end groups of the CA6 peptides will be anionic. Consequently, we tested films with a built-in control, namely a mercaptoundecanoic acid (MUA), an alkane

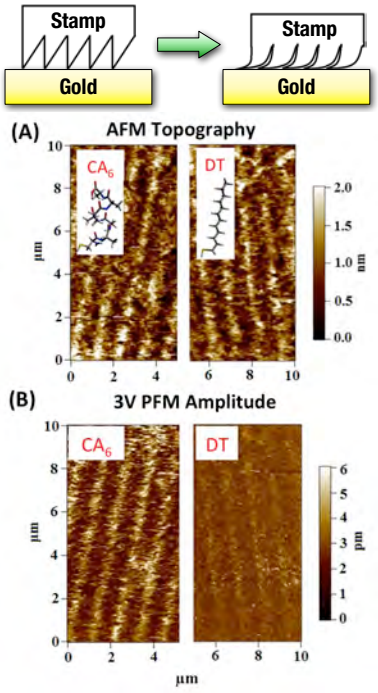

Fig. 7. Patterned self-assembled monolayers of oligopeptide (CA_6) and dodecanethiol (DT), showing similar topography, but much greater piezo response from CA_6.

with carboxylate end groups and comparable height and pKa to CA_6.

Patterned circles of CA6 were deposited onto template-stripped gold surfaces (**Fig. 8a**), followed by deposition of MUA over bare gold regions (**Fig. 8c**). Significantly increased piezoelectric response can be observed comparing the phase (**Fig. 8e**) and amplitude (**Fig. 8g**) of the CA_6 compared to the neighboring MUA regions. Moreover, we deposited MUA patterns (**Fig. 8b**) and compared to the neutralized am-CA_6 in which all carboxylic end groups are converted to the methyl amide substituent. Again, the peptide generates significantly greater piezo-response (**Fig. 8h**) even compared to the electrically charged MUA regions.

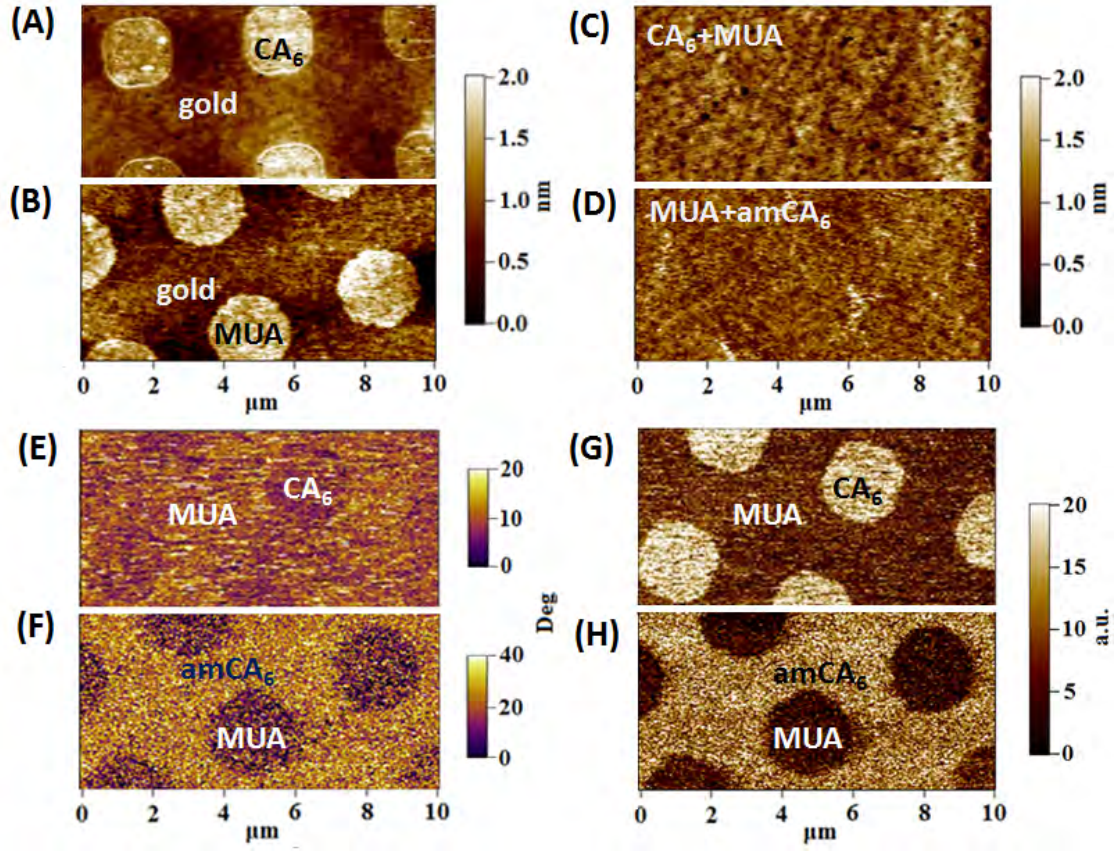

Figure 8. AFM topography, single-frequency PFM phase and amplitude of patterned and mixed monolayers. AFM topography of oligopeptide CA_6 SAM (**A**) and MUA SAM (B) on bare gold, AFM topography of the mixed SAMs CA_6/MUA (C) and MUA/CA_6-am (D), single-frequency PFM phase image of mixed CA_6/MUA (E) MUA/CA_6-am (F), and single-frequency PFM amplitude of a mixed CA_6/MUA (G) and MUA/CA_6-am (H) films with an applied bias of 3V.

While the single-frequency PFM mode used to image the mixed films cannot yield reliable *quantitative* measurements, this technique clearly indicates that PFM deformation observed in CA_6 and CA_6-am patterns ***derives largely from molecular conformational changes*** and not from end-group effects.

To further understand this significant result, we performed DFT calculations on the Cys-$(Ala)_6$ peptides in an α-helical conformation.[5] Under an applied electric field of 1 V/nm, parallel to the molecular dipole moment, the optimized geometry lengthens by 3% (0.25Å), and correspondingly shrinks by 2% (0.20Å) in an anti-parallel field. We predict similar deformations via molecular dynamics, although protein force fields greatly overestimate the distortions (by

factors of ~50). Our results suggest that many proteins are piezoelectric, with continuous linear distortion in response to an electric field, strikingly different from conventional "switches" in light- or redox-driven molecular motors.[10-27]

The measured piezoelectric coefficients of the oligopeptides are in good agreement with our computational predictions and other recent experiments measuring piezoresponse in larger-scale biological materials, including collagen, amyloid fibrils, and individual cells.[28-31] The experimental value is naturally lower than that predicted computationally, partly because of the tilt angle of the molecules on the gold surface, the intrinsic disorder of the SAM, screening of the electric field by ambient water at the tip/surface interface, and inefficient mechanical coupling between the tip and SAM.

Importantly, deposition and patterning of thiol self-assembled monolayers on gold surfaces is facile, creating in intrinsically polar film for PFM characterization. We have found the techniques, namely patterning against bare gold and inert alkanethiols that lead to accurate characterization of nanoscale (~1 nm) films of organic monolayers. This technique is amenable to rapid experimental screening of candidate piezoelectric materials.

Highly Responsive Flexible Piezoelectric Films

While impressive, the nanoscale response of SAM films will not generate significant energy for energy harvesting applications, nor practical devices. The direct piezoelectric effect is the change in surface charge due to an applied force. Because a polarization difference between two regions gives rise to a surface charge on their boundary, and polarization has units of charge per area, the piezoelectric charge per unit force can also be viewed as the change in polarization (dipole moment density) per unit stress, and so the piezocoefficient d can be rewritten as:

$$d = \frac{dQ}{dF} = \frac{d\left(\frac{\mu}{V}\right)}{d\sigma} = \frac{-\mu/V}{K} \qquad (2)$$

in short, the charge (Q) per unit force (F) is equivalent to the concentration of dipole moments μ per unit volume (V) divided by the bulk modulus K.

Equation 2 indicates that by increasing the dipole moment, the fraction of polar molecules in a lattice, and decreasing the bulk modulus, we can obtain large piezoresponse. Previous work has occurred in nonlinear optical (NLO) materials, doping highly polar chromaphores in polymer matrices followed by poling the materials with high field. We can estimate the response of such materials with Equation 2, e.g. a PMMA matrix (K=6.1 GPa) with a 1 M concentration of a dopant with a molecular dipole moment of 10 D, the expected piezocoefficient is 3.3 pC/N in line with previous with reports of NLO materials with piezocoefficients up to 2.5 pC/N. Despite the high polarizations achieved in these materials, the response is low.

Covalent self-assembled multilayers are known to significantly increase the concentration of polar molecules (i.e., essentially to unity).[32-35] Alternatively, a more flexible material could be designed using a foam to achieve a bulk modulus orders of magnitude lower than other materials of similar composition. A foam structure also results in decreased polarization because of the reduced relative density, but this suggests an optimum balance can be found between foam density and piezoelectric response.

We fabricated thin-film (5 mm) foams using commercial polyurethane precursors while incorporating different polar molecular dopants at varying aqueous concentrations. The highest solubility was found for 2-chloro-4-nitroaniline (CNA), but all molecules tested fell on a universal line correlating dipole moment concentration (i.e., Debye • molarity) with measured

piezoelectric response. Characterization was performed by quasi-static force loading, increasing the applied force and measuring electrical current at short-circuit conditions (**Fig. 9**).

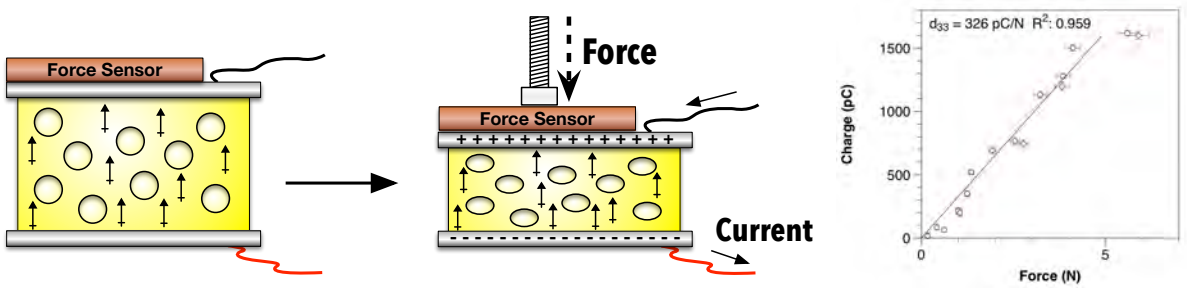

Fig. 9. (left) Schematic of open-cell flexible polyurethane foam doped with polar guest molecules under quasi-static force loading. (right) Increasing applied force generates increased generated charge, with the slope of the calibration line equal to the piezo coefficient (d_{33}).

We find no measureable piezoelectric properties in undoped polyurethane foams, unpoled films of doped polyurethane, or poled films of CNA (which crystallizes into a symmetric, non-piezoelectric crystal structure). Importantly, the response increases with poling field (**Fig. 10**) indicating the fraction of poled CNA guest increases up to ~80 % with an applied field of 40 V/cm, significantly lower than fields used to pole PVDF or perovskite ceramics.

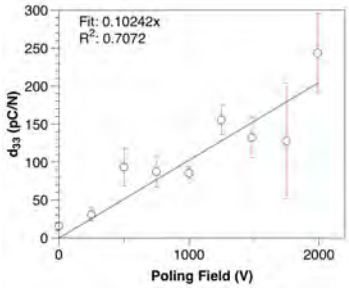

Fig. 10 Measured piezoresponse as a function of applied poling field.

While the polar guest molecules are simply adsorbed into the polymer matrix, we find significant stability to the poled films with >80% piezoresponse persisting beyond 7 days. Further improvement should occur by covalent cross-linking between the polymer matrix and the guests or other strong guest-host interactions after poling.

Importantly, these films, due to the low bulk modulus, are inherently flexible and generate ***immense piezoelectric response >250 pC/N over ten times the generated charge of comparable ZnO and PVDF materials.*** Measured short-circuit currents exceed 0.4 mA/m^2 across a 1.0 cm^2 film. Since we compute the dipole moment of CNA to be only 7.69 D, the response should increase with more polar guests and higher loading concentrations, easily exceeding champion perovskite ceramics such as PZT even with non-piezoelectric molecules. The combination of piezo-active molecular units and self-assembled multi-layers should create a new realm of energy harvesting materials and nanoscale artificial muscles.

References:

(1) Paturle, A.; Graafsma, H.; Sheu, H. S.; Coppens, P.; Becker, P. "Measurement of the Piezoelectric Tensor of an Organic Crystal by the X-Ray Method: The Nonlinear Optical Crystal 2-Methyl 4-Nitroaniline.," *Physical Review B* **1991**, *43*, 14683.

(2) Werling, K. A.; Hutchison, G.; Lambrecht, D. S. "Piezoelectric Effects of Applied Electric Fields on Hydrogen-Bond Interactions: First-Principles Electronic Structure Investigation of Weak Electrostatic Interactions," *Journal Of Physical Chemistry Letters* **2013**, *4*, 1365.

(3) Werling, K. A.; Griffin, M.; Hutchison, G. R.; Lambrecht, D. S. "Piezoelectric Hydrogen Bonding: Computational Screening for a Design Rationale," *Journal Of Physical Chemistry A* **2014**, 140325144029007.

(4) Quan, X.; Marvin, C. W.; Seebald, L.; Hutchison, G. R. “Single-Molecule Piezoelectric Deformation: Rational Design from First-Principles Calculations,” *The Journal of Physical Chemistry C* **2013**, *117*, 16783.
(5) Quan, X.; Madura, J. D.; Hutchison, G. “Self-Assembled Molecular Monolayer Piezoelectrics Using Oligopeptides,” *Submitted to Nano Lett* **2014**.
(6) Balke, N.; Bdikin, I.; Kalinin, S. V.; Kholkin, A. L. “Electromechanical Imaging and Spectroscopy of Ferroelectric and Piezoelectric Materials: State of the Art and Prospects for the Future,” *Journal of the American Ceramic Society* **2009**, *92*, 1629.
(7) Kalinin, S. V.; Mirman, B.; Karapetian, E. “Relationship between Direct and Converse Piezoelectric Effect in a Nanoscale Electromechanical Contact,” *Physical Review B: Condensed Matter and Materials Physics* **2007**, *76*, 212102.
(8) Kalinin, S. V.; Rodriguez, B. J.; Jesse, S.; Seal, K.; Proksch, R.; Hohlbauch, S.; Revenko, I.; Thompson, G. L.; Vertegel, A. A. “Towards Local Electromechanical Probing of Cellular and Biomolecular Systems in a Liquid Environment,” *Nanotechnology* **2007**, *18*, 424020.
(9) Kalinin, S.; Shao, R.; Bonnell, D. “Local Phenomena in Oxides by Advanced Scanning Probe Microscopy,” *Journal of the American Ceramic Society* **2005**, *88*, 1077.
(10) Bustamante, C.; Chemla, Y.; Forde, N.; Izhaky, D. “Mechanical Processes in Biochemistry,” *Annual Review of Biochemistry* **2004**, *73*, 705.
(11) Harada, N.; Saito, A.; Koumura, N.; Uda, H.; Delange, B.; Jager, W.; Wynberg, H.; Feringa, B. “Chemistry of Unique Chiral Olefins .1. Synthesis, Enantioresolution, Circular Dichroism, and Theoretical Determination of the Absolute Stereochemistry of Trans- and Cis-1,1&Apos;,2,2&Apos;,3,3&Apos;,4,4&Apos;-Octahydro-4,4&Apos;-Biphenanthrylidenes,” *Journal Of The American Chemical Society* **1997**, *119*, 7241.
(12) Harada, N.; Saito, A.; Koumura, N.; Roe, D.; Jager, W.; Zijlstra, R.; Delange, B.; Feringa, B. “Chemistry of Unique Chiral Olefins .2. Unexpected Thermal Racemization of Cis-1,1&Apos;,2,2&Apos;,3,3&Apos;,4,4&Apos;-Octahydro-4,4&Apos;-Biphenanthrylidene,” *Journal Of The American Chemical Society* **1997**, *119*, 7249.
(13) Feringa, B. L. “The Art of Building Small: From Molecular Switches to Molecular Motors,” *Journal of Organic Chemistry* **2007**, *72*, 6635.
(14) Pollard, M. M.; Lubomska, M.; Rudolf, P.; Feringa, B. L. “Controlled Rotary Motion in a Monolayer of Molecular Motors,” *Angewandte Chemie, International Edition in English* **2007**, *46*, 1278.
(15) Browne, W. R.; Feringa, B. L. “Making Molecular Machines Work,” *Nature Nanotechnology* **2006**, *1*, 25.
(16) Eelkema, R.; Pollard, M.; Vicario, J.; Katsonis, N.; Ramon, B.; Bastiaansen, C.; Broer, D.; Feringa, B. “Nanomotor Rotates Microscale Objects,” *Nature (London, United Kingdom)* **2006**, *440*, 163.
(17) Van Delden, R.; Ter Wiel, M.; Pollard, M.; Vicario, J. “Unidirectional Molecular Motor on a Gold Surface,” *Nature* **2005**.
(18) Saha, S.; Leung, K. C. F.; Nguyen, T. D.; Stoddart, J. F.; Zink, J. I. “Nanovalves,” *Advanced Functional Materials* **2007**, *17*, 685.
(19) Brough, B.; Northrop, B.; Schmidt, J.; Tseng, H.; Houk, K.; Stoddart, J.; Ho, C. “Evaluation of Synthetic Linear Motor-Molecule Actuation Energetics,” *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 8583.

(20) Dichtel, W. R.; Heath, J. R.; Stoddart, J. F. "Designing Bistable [2] Rotaxanes for Molecular Electronic Devices," *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **2007**, *365*, 1607.
(21) Horinek, D.; Michl, J. "Surface-Mounted Altitudinal Molecular Rotors in Alternating Electric Field: Single-Molecule Parametric Oscillator Molecular Dynamics," *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102*, 14175.
(22) Saha, S.; Flood, A. H.; Stoddart, J. F.; Impellizzeri, S.; Silvi, S.; Venturi, M.; Credi, A. "A Redox-Driven Multicomponent Molecular Shuttle," *Journal Of The American Chemical Society* **2007**, *129*, 12159.
(23) Pease, A.; Jeppesen, J.; Stoddart, J.; Luo, Y. "Switching Devices Based on Interlocked Molecules," *Accounts Of Chemical Research* **2001**.
(24) Shipway, A.; Willner, I. "Electronically Transduced Molecular Mechanical and Information Functions on Surfaces," *Accounts Of Chemical Research* **2001**.
(25) Feringa, B. "In Control of Motion: From Molecular Switches to Molecular Motors," *Accounts Of Chemical Research* **2001**.
(26) Kelly, T. "Progress toward a Rationally Designed Molecular Motor," *Accounts Of Chemical Research* **2001**.
(27) Collin, J.; Dietrich-Buchecker, C.; Gavina, P. "Shuttles and Muscles: Linear Molecular Machines Based on Transition Metals," *Accounts Of Chemical Research* **2001**.
(28) Nikiforov, M. P.; Thompson, G. L.; Reukov, V. V.; Jesse, S.; Guo, S.; Rodriguez, B. J.; Seal, K.; Vertegel, A. A.; Kalinin, S. V. "Double-Layer Mediated Electromechanical Response of Amyloid Fibrils in Liquid Environment," *ACS Nano* **2010**, *4*, 689.
(29) Kalinin, S. V.; Rodriguez, B. J.; Jesse, S.; Karapetian, E.; Mirman, B.; Eliseev, E. A.; Morozovska, A. N. "Nanoscale Electromechanics of Ferroelectric and Biological Systems: A New Dimension in Scanning Probe Microscopy," *Annual Review Of Materials Research* **2007**, *37*, 189.
(30) Kholkin, A.; Amdursky, N.; Bdikin, I.; Gazit, E.; Rosenman, G. "Strong Piezoelectricity in Bioinspired Peptide Nanotubes," *ACS Nano* **2010**, *4*, 610.
(31) Kalinin, S. V.; Rodriguez, B. J.; Jesse, S.; Thundat, T.; Gruverman, A. "Electromechanical Imaging of Biological Systems with Sub-10 Nm Resolution," *Applied Physics Letters* **2005**, *87*, 053901.
(32) Yitzchaik, S.; Marks, T. "Chromophoric Self-Assembled Superlattices," *Accounts Of Chemical Research* **1996**, *29*, 197.
(33) Zhu, P.; Van Der Boom, M.; Kang, H.; Evmenenko, G.; Dutta, P.; Marks, T. "Realization of Expeditious Layer-by-Layer Siloxane-Based Self-Assembly as an Efficient Route to Structurally Regular Acentric Superlattices with Large Electro-Optic Responses," *Chemistry Of Materials* **2002**, *14*, 4982.
(34) Van Der Boom, M.; Zhu, P.; Evmenenko, G.; Malinsky, J.; Lin, W.; Dutta, P.; Marks, T. "Nanoscale Consecutive Self-Assembly of Thin-Film Molecular Materials for Electrooptic Switching. Chemical Streamlining and Ultrahigh Response Chromophores," *Langmuir* **2002**, *18*, 3704.
(35) Van Der Boom, M.; Richter, A. G.; Malinsky, J.; Lee, P.; Armstrong, N.; Dutta, P.; Marks, T. "Single Reactor Route to Polar Superlattices. Layer-by-Layer Self-Assembly of Large-Response Molecular Electrooptic Materials by Protection-Deprotection," *Chemistry Of Materials* **2001**, *13*, 15.

Personnel Supported:

Faculty:	Prof. Geoffrey Hutchison (1 month support)
Graduate Students:	Xinfeng Quan (Ph.D., September 2013, now an instructor at Sichuan University - Pittsburgh Institute)
	Paula Hoffmann (Ph.D., April 2015)
	Christopher Marvin

Publications/Accepted or In Print (partially or fully supported by this project):

1) Keith A. Werling, Geoffrey R. Hutchison, Daniel S. Lambrecht. "Piezoelectric Effects of Applied Electric Fields on Hydrogen-Bond Interactions: First Principles Electronic Structure Investigation of Weak Electrostatic Interactions." *J. Phys. Chem. Lett.* **2013** vol. 4(9) pp. 1365-1370.
2) Xinfeng Quan, Christopher W. Marvin, Leah Seebald, Geoffrey R. Hutchison. "Single-Molecule Piezoelectric Deformation: Rational Design from First-Principals Calculations." *J. Phys. Chem. C* **2013** vol. 117 pp. 16783-16790.
3) Keith A. Werling, Maryanne Griffin, Geoffrey R. Hutchison, and Daniel S. Lambrecht. "Piezoelectric Hydrogen Bonding: Computational Screening for a Design Rationale." *J. Phys. Chem. A* **2014** vol. *118(35)*, pp 7404–7410.
4) Xinfeng Quan. *Single molecule piezoelectrics and ferroelectrics: from theory to experiment.* Ph.D. Dissertation **2014**. http://d-scholarship.pitt.edu/20196/

Publications Submitted or In Preparation (partially or fully supported by this project):

5) Xinfeng Quan, Jeffry D. Madura, Geoffrey R. Hutchison. "Self-Assembled Molecular Monolayer Piezoelectrics Using Oligopeptides." *Submitted*.
6) Xinfeng Quan, Geoffrey R. Hutchison. "Single Molecule Ferroelectrics: Conformational Hysteresis from Applied Electric Fields." *Submitted*.
7) Christopher W. Marvin, Cameron Selby, Anjali Premkumar, Geoffrey R. Hutchison. "Large Single-Molecule Piezoelectric Deformation in Substituted Helicenes." *In Preparation.*
8) Michael J. Moody, Geoffrey R. Hutchison. "Molecularly Doped Polymer Foams with Immense Piezoelectric Response." *In Preparation.*

Interactions/Transitions (partially or fully supported by this project):

1) Argonne-Northwestern Solar Energy Research Center, Northwestern University, Oct. 4, 2012. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
2) Department of Chemistry and Chemical Biology, Cornell University, Oct. 15, 2012. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
3) Center for Organic Photonics and Electronics, Georgia Tech, Oct. 29, 2012. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
4) Department of Chemistry, Johns Hopkins University, Nov. 6, 2012. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
5) Department of Chemistry, Carnegie Mellon University, March 7, 2013. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
6) Department of Chemistry, University of Minnesota, March 14, 2013. "Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More"
7) Pitt Quantum Initiative: Quantum Matter Symposium, April 18-19, 2013. "Quantum Design for Molecular Materials: Rapidly Finding Improved Properties"

8) Department of Chemistry, Messiah College, May 2, 2013. “Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More”
9) Center for Polymers and Organic Solids, UC Santa Barbara, May 7, 2013. “Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More”
10) Gordon Research Conference, Electron Donor-Acceptor Interactions: August 5-10, 2012 “Donor-Acceptor Molecular Piezoelectrics: Electromechanical Materials From the Bottom Up”
11) American Chemical Society National Meeting Fall 2012 “Single molecule piezoelectrics: Theory and experiment”
12) Department of Chemistry, University of Pittsburgh, Sep. 26, 2013 “Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More”
13) Department of Chemistry and Biochemistry, UC San Diego, October 11, 2013 “Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More”
14) Department of Chemistry, University of Illinois at Urbana-Champaign, November 6-7, 2013 “Rational Design of Molecular Materials: Molecular Springs, Solar Cells & More”
15) Department of Chemistry, New York University, May 7, 2015, “Rational Design of Molecular Springs”

New Discoveries, Inventions, or Patent Disclosures:

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1.

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Geoffrey R. Hutchison

Program Manager

The AFOSR Program Manager currently assigned to the award

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Abstract

There is a critical need for efficient energy harvesting materials to use ubiquitous but wasted mechanical energy. There is also a simultaneous need for micro- and nano-electronic energy generation and conversion for self-powered sensors, haptic displays, and responsive shape-changing materials. With this project, we have established that dramatic improvements can be found in piezoelectric materials designed from the geometric conformational change in single molecules, driven by electric field gradients. This project designed accurate, efficient quantum chemical methods to efficiently predict the piezoresponse of conventional hydrogen-bonded organic crystals and polymers e.g., polyvinylidene difluoride (PVDF). Using these methods, we determined a theoretical maximum for conventional organic piezoelectrics and devised molecular springs with predicted response far exceeding ZnO or PVDF. Moreover, investigating different molecular scaffolds, we designed single-molecule ferroelectrics with stable hysteresis and piezoelectric response predicted on par with champion perovskites. Our computational methods demonstrate the strong potential for molecular piezoelectrics, with high dipole moment, high polarizability, and low force constant vibrational modes as key properties for future designs. We experimentally demonstrated this potential with the first measurements of the piezoelectric response of single molecular monolayers as an effective experimental screening method for future materials. Moreover, using a polyurethane foam matrix, we embedded the polar molecule 2-chloro-4-nitroaniline and demonstrated flexible piezoelectric materials

exceeding 250 pC/N, over ten times the response of ZnO and PVDF.

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2) Xinfeng Quan, Christopher W. Marvin, Leah Seebald, Geoffrey R. Hutchison. “Single-Molecule Piezoelectric Deformation: Rational Design from First-Principals Calculations.” J. Phys. Chem. C 2013 vol. 117 pp. 16783-16790.
3) Keith A. Werling, Maryanne Griffin, Geoffrey R. Hutchison, and Daniel S. Lambrecht. “Piezoelectric Hydrogen Bonding: Computational Screening for a Design Rationale.” J. Phys. Chem. A 2014 vol. 118(35), pp 7404–7410.
4) Xinfeng Quan. Single molecule piezoelectrics and ferroelectrics: from theory to experiment. Ph.D. Dissertation 2014. http://d-scholarship.pitt.edu/20196/

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LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

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Equipment/Facilities			
Supplies			
Total			

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Appendix Documents

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